

PATENT SPECIFICATION

1003,310



NO DRAWINGS

1003,310

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COMPLETE SPECIFICATION

Bleaching processes and compositions

We, UNILEVER LIMITED, a Company registered under the laws of Great Britain, of Port Sunlight, in the County of Chester, England do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This Specification relates to bleaching processes and compositions, and particularly to modifications of the bleaching processes and composition described in our British Patent No. 855,735.

The above patent describes and claims a bleaching process in which textile materials are bleached using an aqueous solution of hydrogen peroxide and a reactive acyl organoamide. It also describes and claims bleaching compositions which comprise an inorganic per-salt and a reactive acyl organoamide. The acyl organoamides are compounds of the formula



in which RCO is a carboxylic acyl radical, R₁ is a second acyl radical, and R₂ is any suitable organic radical as determined by the behaviour of the compound in the test described below. Suitable acyl organoamides have an activating effect upon the bleaching activity in inorganic per-salts at temperatures of about 50°—60°C, and are simply and conveniently characterised by a test in which a persalt and the amide are heated together in water and the vigorous bleaching agent thus produced is estimated by its ability to liberate iodine from potassium iodide solution at 0°C. For convenience this test is reproduced below.

TEST

A test solution is prepared by dissolving the following materials in 1000 ml. distilled water:

Sodium pyrophosphate	Na ₄ P ₂ O ₇ .10H ₂ O	2.5 g.
Sodium perborate	NaBO ₃ .H ₂ O ₂ .3H ₂ O	0.615 g.
(having 10.4% available oxygen)		45
Sodium dodecylbenzene sulphonate		0.5 g.
(the dodecyl group being that derived from tetrapropylene)		

To this solution at 60°C. is added an amount of amide such that for each atom of available oxygen present one equivalent of amide is introduced. A water-insoluble amide or one which is liquid at 60°C. or will disperse into the solution easily is added directly to the test solution, but other amides are first dissolved in 10 ml. ethyl alcohol and then added to a test solution prepared using 990 ml. distilled water.

The mixture obtained by addition of the amide is vigorously stirred and maintained at 60°C. After 5 minutes from the addition a 100 ml. portion of the solution is withdrawn and immediately pipetted on to a mixture of 250 g. cracked ice and 15 ml. glacial acetic acid. Potassium iodide (0.4 g.) is then added and the liberated iodine is immediately titrated with 0.1 N Sodium thiosulphate solution with starch as indicator until the first disappearance of the blue colour.

An amide which is suitable as an activator for hydrogen peroxide (or persalt) in low temperature bleaching is one which in this test gives a titre of at least 1.5 ml.

It has now been discovered that certain acyl sulphonamides have an activating effect on the bleaching activity of inorganic persalts at the temperatures (about 50°—60°C) which are commonly found in domestic washing machines.

The processes of this invention are ones which textile materials are bleached using an aqueous solution of hydrogen peroxide and a reactive acyl sulphonamide. The compositions of this invention which are suitable for use in

these processes comprise an inorganic persalt and a reactive acylsulphonamide.

By "reactive acyl sulphonamide" is meant a compound of the formula:



in which RCO - is a carboxylic acyl radical, $\text{R}'\text{SO}_2$ - is an organosulphonyl radical, and R'' is any suitable organic radical except a carboxylic acyl radical attached directly to the nitrogen, as determined by the behaviour of the acyl sulphonamide in the above test in that it must have a titre of at least 1.5 ml. 0.1 N sodium thiosulphate. R' can for example be an alkyl, aryl or substituted alkyl group wherein the substituents may include a further sulphonyl group and a further carboxylic acyl group. Preferably R' is methyl or phenyl. R'' is preferably ethyl or phenyl. The radical RCO is preferably the acetyl or benzoyl radical. Any two of the radicals RCO , R' and R'' can be linked together, thus forming a divalent radical, which with the nitrogen is a heterocyclic group.

A list of some reactive acyl sulphonamides is given below, together with the titre which each gives in the test described above.

Compound	Titre (ml.)
1 N-Methyl - N-benzoyl-methanesulphonamide	5.6
30 2 N-Phenyl - N-acetyl - benzene-sulphonamide	3.9
3 N,N-Ethylene - di(N-acetyl - methanesulphonamide)	5.6
4 Ethylene-di(N-phenyl - N-acetyl - sulphonamide)	2.7
35 5 N-Methyl - N-benzoyl - benzene-sulphonamide	4.9

Other suitable reactive sulphonamides are:

40 6 N-Methyl - N-acetyl - benzenesulphonamide,
7 N-Methyl - N-acetyl - <i>p</i> -toluenesulphonamide,
8 N-Methyl - N-benzoyl - <i>p</i> -toluenesulphonamide,
45 9 N-Phenyl - N-acetyl - methanesulphonamide,
10 N,N ¹ -Dimethyl - N,N ¹ diacetylsulphamide,
11 N-Phenyl - N-benzoyl - benzenesulphonamide,
50 12 N-Phenyl - N-acetyl - <i>p</i> -toluenesulphonamide,
13 N-Phenyl - N-benzoyl - <i>p</i> -toluenesulphonamide,
55 14 N,N-Ethylene - di(N-acetyl-benzenesulphonamide),

15 N-Methyl - N-acetyl - methanesulphonamide, and
16 N-Phenyl - N-benzoyl - methanesulphonamide

These sulphonamides which are numbered 1, 3, 4, 8, 10, 12, 14 and 15 are novel and have been prepared by standard methods.

In the processes of the invention the hydrogen peroxide can be added as such directly to the bleaching bath which is to be used, but preferably it is liberated from an inorganic persalt. The inorganic persalts used in such processes or in the compositions of the invention are those which give rise to hydrogen peroxide when dissolved in water, and suitable compounds are alkali metal perborates, percarbonates, perpyrophosphates and persilicates. Such salts are believed to contain hydrogen peroxide of crystallisation and may thus not be regarded as true persalts.

Preferably the bleaching compositions of the invention contain from $\frac{1}{4}$ to 4, and especially $\frac{1}{2}$ to $1\frac{1}{2}$, reactive sulphonamide groups for each atom of available oxygen in the persalt used, and in the bleaching processes this ratio of sulphonamide to available oxygen is employed.

In practice the processes of the invention are carried out under alkaline conditions, especially at pH of between 8 and 11 in order to enable the hydrogen peroxide (or persalt) to form the agent effective in low temperature bleaching. Once this has been formed the bath can be converted to acid conditions if desired. Accordingly it is also preferable for the bleaching compositions of the invention to contain sufficient of an alkaline substance to provide these pH conditions when the composition is used. Suitable alkaline materials are alkali metal carbonates, phosphates and silicates: the phosphates can be orthophosphates or water-soluble condensed phosphates, for instance tripolyphosphates and pyrophosphates.

Other materials can be included in the bleaching processes and compositions, and it is particularly suitable to incorporate a detergent, so that the bleaching process takes place simultaneously with a washing process. Organic detergents which can be incorporated in the bleaching bath or composition are either soaps or soapless detergents, for instance an alkylaryl sulphonate or an alkyl sulphate. Detergent bleaching compositions will in practice also contain conventional detergent adjuncts, for example alkali metal sulphates, alkaline substances such as those mentioned above, sodium carboxymethyl cellulose, and fluorescent brightening agents. Generally a detergent bleaching composition will contain from 10 to 50% by weight of organic detergent.

Materials which can be bleached by the processes of the invention are those which can be bleached with persalts, for instance, stained cotton fabrics and other stained or soiled fabrics and fibres.

Best results in bleaching according to the invention are obtained under conditions of effective agitation such as exist, for instance, in a washing machine.

5 The invention is illustrated by the following Example in which percentages of matter are percentages by weight.

EXAMPLE

10 Four bleaching solutions were prepared containing:

15 0.054% sodium dodecyl benzene sulphonate
0.018% coconut mono-ethanolamide
0.115% sodium tripolyphosphate
0.045% sodium sulphate
0.029% anhydrous alkaline sodium silicate
0.004% sodium carboxymethylcellulose
0.032% sodium perborate tetrahydrate.

To each freshly-prepared solution was added a reactive sulphonamide in the concentration as given in the table below.

20 A length of cotton cloth was stained by immersion in boiling tea extract for one hour. It was then thoroughly rinsed, dried and cut into pieces whose % reflectances were measured in a Hunter reflectometer using the blue filter. The % reflectance of the test pieces was measured again after bleaching. The bleach obtained was expressed as the difference in the two % readings on each test-piece.

25 A piece of stained cloth was immersed in each of the freshly-prepared bleaching solutions at 60°C. for 10 minutes with stirring. The cloths were then removed from the solutions, rinsed 3 times in distilled water, ironed and their reflectance measured. The results are given in the following table.

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Sulphonamide	Concn. of sulphonamide in solution (%)	Increase in % reflectance	Increase in % reflectance in the absence of sulphonamide (Control)
N-methyl-N-benzoyl-methanesulphonamide	0.043	16.9	12.7
N-phenyl-N-acetyl-benzenesulphonamide	0.055	19.7	15.9
N-methyl-N-benzoyl-benzenesulphonamide	0.055	20.0	13.3
N,N-ethylene-di (N-acetyl-methanesulphonamide)	0.030	13.5	10.1

These results show that the acyl sulphonamide conferred better bleaching properties.

WHAT WE CLAIM IS:—

1. A process in which textile materials are bleached using an aqueous solution of hydrogen peroxide and a reactive acyl sulphonamide as hereinbefore defined.

40 2. A process as claimed in Claim 1 in which the hydrogen peroxide is liberated in the solution from an inorganic persalt.

45 3. A process as claimed in either Claim 1 or 2 in which the aqueous solution is at a pH of between 8 and 11.

50 4. A process as claimed in any preceding claim in which the amide is present in amount corresponding to from $\frac{1}{2}$ to 4 reactive sulphonamide groups for each atom of available oxygen.

55 5. A process as claimed in any preceding claim in which the sulphonamide is an acetyl sulphonamide.

6. A process as claimed in any one of Claims 1—4 in which the sulphonamide is N-methyl - N-benzoyl - methanesulphonamide.

60 7. A process as claimed in any one of Claims 1—4 in which the sulphonamide is N-phenyl - N-acetyl - benzenesulphonamide.

8. A process as claimed in any one of Claims 1—4 in which the sulphonamide is N-methyl - N-benzoyl - benzenesulphonamide.

65 9. A process according to claim 1 for bleaching textile materials using a reactive acyl sulphonamide substantially as described in the Example.

10. A bleaching composition comprising an inorganic persalt and a reactive acyl sulphonamide as hereinbefore defined.

70 11. A composition as claimed in Claim 10 containing an alkaline material.

12. A composition as claimed in Claim 10 or 11 containing an organic detergent.

75 13. A composition as claimed in any one of Claims 10—12 in which the amide is present in amount corresponding to from $\frac{1}{2}$ to 4 reactive sulphonamide groups for each atom of available oxygen.

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14. A composition as claimed in any one of Claims 10—13 in which the sulphonamide is an acetyl sulphonamide.

5 15. A bleaching composition according to claim 10 containing a reactive acyl sulphonamide substantially as described in the Example.

16. A process for bleaching textile materials in which there is used a bleaching composition as claimed in any one of Claims 10—15. 10

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